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Fluorocarbon Resins for Coatings and Inks

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83.1 General

The commercially important fluorocarbon resins are based upon a handful of fluorinated monomers, as indicated in Table 83.1. From these basic building blocks, a wide variety of polymer products can be produced, especially when copolymerization with other, nonfluorinated monomers is a possibility.

Besides polytetrafluoroethylene (PTFE) "coatings" — which are prepared by a high temperature sintering process and which are not considered in this chapter — the most widely used fluorocarbon coatings are based on poly(vinylidene fluoride) (PVDF) homopolymer. Typical PVDF coatings require a high temperature bake and are applied on primed metal substrates by a coil coating or spray technique. They are commonly used in high-end architectural applications such as skyscraper curtain walls and other wall panel systems, window profiles, and commercial and residential metal roofing. The first commercial grade of PVDF for coatings, KYNAR 500®, was introduced in 1965 by the Pennsalt Company. This same resin grade continues to be sold today by Arkema, Inc., under a worldwide licensing program.

Another commercially important class of fluorocarbon resins, fluorinated ethylene vinyl ether (FEVE) polymers, was introduced in the early 1980s by Asahi Glass, under the Lumiflon® trademark. FEVE products continue to enjoy their greatest success in the Far East, especially for site-applied (air-dry) applications such as industrial maintenance topcoats. Both PVDF and FEVE coatings combine superior weatherability with excellent protective and barrier properties. They are, therefore, able to simultaneously function as decorative and functional finishes.

Among the other types of fluorocarbon resins used in coatings, fluorinated acrylics are also used in significant volumes and have a long history. They are chiefly used as surface treatment agents, for applications where low surface energy is sought, e.g., for water and oil repellency.

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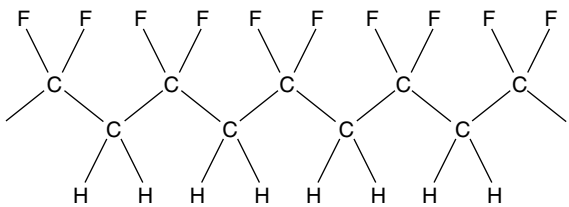
TABLE 83.1 Fluorinated Monomers Used in the Manufacture of Common Fluororesins Used in Coatings

Monomer Acronym	Common Monomer Name	Molecular Formula	Principal Use in Fluororesins for Coatings
TFE	Tetrafluoroethylene	$CF_2=CF_2$	Comonomer for FEVE resins and PVDF copolymers; also coating additives
VDF or VF_2	Vinylidene fluoride	$CF_2=CH_2$	PVDF homopolymer and copolymers
CTFE	Chlorotrifluoroethylene	$CFCl=CF_2$	Comonomer for FEVE resins and PVDF copolymers
HFP	Hexafluoropropylene	$CF_3CF=CF_2$	Comonomer for PVDF copolymers
—	Fluorinated decyl acrylate	n-$C_8F_{17}CH_2CH_2O$-COCH=CH_2	Comonomer for fluorinated acrylics

83.2 Poly(Vinylidene Fluoride) (PVDF) Resins for Coatings

PVDF for coatings applications is produced by a high pressure emulsion polymerization process. Vinylidene fluoride monomer normally polymerizes in a head-to-tail fashion, so the idealized structure of PVDF resin has alternating $–CH_2–$ and $–CF_2–$ groups:



Poly(vinylidene fluoride) (PVDF)

This highly regular structure, and high fluorine content (59 wt% fluorine), contributes to the excellent chemical and photochemical stability of the PVDF resin. At the same time, because there is substantial polarity along the PVDF backbone, the resin can undergo favorable thermodynamic interactions with a variety of solvents and with certain other polymers (chiefly those with high levels of carbonyl groups). This property is exploited by paint formulators, in the choice of co-resins and solvents that are used in PVDF formulations.

Compatible acrylic co-resins are widely used in PVDF paint formulations, to provide certain features such as pigment wetting and enhanced adhesion, which cannot be supplied by the relatively inert PVDF resin. Common acrylics used include poly(methyl methacrylate) (pMMA) grades and methyl methacrylate-ethyl acrylate copolymers. Acrylic levels of 20 to 30 wt% on total binder are generally used — these provide the desired performance enhancements, without too greatly compromising key PVDF properties such as weatherability, flexibility, and chemical resistance. While thermoplastic acrylics perform well in these systems, low levels of acrylic cross-linking are sometimes used by paint formulators to achieve specific performance enhancements, such as early MEK resistance for coil coatings.

Typical PVDF paint formulations generally contain one or more "latent solvents" that have good solvency for PVDF and the co-resin under high temperature bake conditions, and so promote an intimate resin alloy structure in the final coating film. Like pure PVDF homopolymer, PVDF-acrylic alloys at 70 to 80% PVDF are semicrystalline. The exact microscopic organization of the crystalline structures in these alloys depends on a variety of factors, including the cooling rate. However, in general, the crystallites act as labile cross-links, enhancing various coating properties, including chemical and solvent resistance, hardness, and barrier properties. To achieve the proper morphology, bake temperatures well above the PVDF 170°C melt temperature are used. This requirement limits the use of paints based on PVDF homopolymer to heat-insensitive substrates such as metals.

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Most PVDF paints are formulated for application either by roll or spray coating. The substrates for spray coating are typically aluminum extrusions. Roll-coat application of PVDF paints is normally done on coil (precoated metal) lines, using a variety of metal substrates, including steel, galvanized steel, Galvalume®, and aluminum.

Historically, PVDF coatings have been used to meet the most demanding specifications for architectural products — such as the American Architectural Manufacturers Association (AAMA) specifications. For instance, the recent AAMA 2605 specification for spray-coated aluminum extrusions and panels calls for 10-year Florida gloss and color retention. To achieve this ambitious goal, paint formulators combine proven PVDF resin technology with carefully selected weatherable pigments, typically highly stable metal-oxide-type pigments.

While most PVDF coating applications continue to use solvent dispersions, a variety of technical alternatives have also been developed over the years, based on vinylidene fluoride resins. For baked applications, special PVDF homopolymer grades can be used to make PVDF powder coatings and waterborne baked coatings. When formulated at ratios like those of the standard solvent paints, the powder coating and waterborne approaches achieve performance, including weathering performance, equivalent to that of the solvent paints.

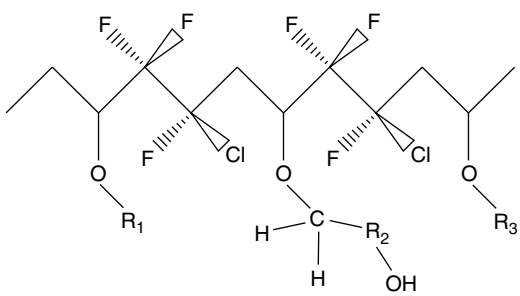
Neat PVDF resins in powdered form, and other neat fluoropolymers, are also used in limited quantities to make functional powder coatings, especially for the chemical process industry.

Copolymers of vinylidene fluoride with other fluorinated monomers have lower crystallinity and higher solubility in various solvents than PVDF homopolymer. These can be used to make solvent air-dry paints, suitable for use in building restoration, and for repair and touch up of PVDF paints. [These paints, however, have high volatile organic compound (VOC) levels.] Vinylidene fluoride copolymers are also used in niche ink and printing applications. More recently, PVDF copolymer grades have been used to make water-based latex dispersions. These can be used as the base resin for waterborne paints with very low VOC levels, for instance, for industrial maintenance coatings, or for architectural coatings for objects such as PVC window frames.

Another recent trend is the use of PVDF films as paint substitutes. PVDF paint films have compositions similar to traditional PVDF paints and are prepared by solvent casting or extrusion processes. They typically have a multiple layer structure and can be used with heat-sensitive substrates, for instance, in automotive and other transportation industry applications.

83.3 Fluorinated Ethylene Vinyl Ether (FEVE) Resins for Coatings

The idealized structure of an FEVE copolymer is an alternating copolymer of a highly fluorinated monomer and nonfluorinated vinyl ether monomers.



Commercial FEVE products are typically based on chlorotrifluoroethylene (CTFE), as shown in the above structure, or tetrafluoroethylene (TFE). Electronic induction effects from the fluorine atoms are

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thought to confer photochemical stability to adjacent vinyl ether portions of the FEVE backbone, greatly enhancing weatherability compared to nonfluorinated ethers.

Some resin suppliers manufacture FEVE-type resins based on vinyl ester monomers rather than on vinyl ether monomers. However, the vinyl ester resins are generally understood to have inferior properties, including inferior weatherability.

Normally, a combination of vinyl ether monomers is used in order to attain a specific balance of properties. Besides using nonfunctional vinyl ether monomers such as vinyl cyclohexyl ether, vinyl ethers with functional groups on the side chain are used in measured proportions. These groups provide sites for cross-linking and can be advantageous to enhance pigment wetting, compatibility with cross-linkers, and adhesion. FEVE resins are amorphous, so unlike the case of PVDF coatings, cross-linking is normally needed for full coating property development. Most commonly, hydroxy functional monomers such as hydroxybutyl vinyl ether are used, giving resins that can be cross-linked with isocyanate or melamine cross-linkers. However, other functional groups such as acid or epoxy groups can be incorporated into the FEVE resin as well, alone or in combination.

FEVE resins can be manufactured by a number of routes (solution polymerization, emulsion polymerization, etc.). Commercial FEVE resins are most commonly supplied in a solvent, but powder and waterborne grades are also available.

Hydroxy functional FEVE solution polymers are used with aliphatic polyisocyanate cross-linkers [e.g., hexamethylene diisocyanate (HDI) isocyanurates] to make two-component air-dry coatings. The reaction of the hydroxyl groups on the FEVE resin with cross-linker isocyanate groups makes urethane linkages, under ambient conditions. This chemistry is ideal for site-applied applications such as bridges and causeways, storage tanks, and building refinishing.

For baked systems, blocked isocyanate cross-linkers such as caprolactam-blocked isophorone diisocyanate can be used (this chemistry is often used in powder coating systems). Aminoplast cross-linkers such as melamines can also be used.

83.4 Fluorinated Acrylics

Fluorinated acrylics are typically solution polymers, prepared by copolymerizing acrylic monomers having long, perfluorinated side chains, along with other, nonfluorinated acrylic monomers. By careful adjustment of the composition, fluorinated acrylics form films with $–CF_3$ groups from the side chains aligned on the surface, through side chain crystallization. The surface $–CF_3$ groups give coatings with an extremely low surface energy, down to 8 dyn/cm. Such surfaces are not only water repellent but are also oleophobic (oil-repellent). As such, they are useful for fabric treatments, as anti-graffiti coatings, and in kitchen and industrial workplace applications.

To maintain the favorable surface properties of fluorinated acrylic coatings, some kind of cross-linking chemistry is often incorporated into the resin backbone. Nevertheless, the durability of fluorinated acrylics is normally not equal to that of other common highly fluorinated coatings.

83.5 Other Fluorinated Resins for Coatings and Inks

As the various chapters in the bibliography reference works attest, there is a wide variety of fluoropolymers commercially available, each with a unique combination of chemical and physical properties. Besides the larger volume products described above, many other fluoropolymers have been considered for specialized niche applications. Among these are the following:

- Perfluorinated elastomeric resins (e.g., tetrafluoroethylene-hexafluoropropylene copolymers) for situations where excellent chemical resistance, including alkali resistance, is required.
- Low molecular weight, mobile perfluoroether resins for the protection of stone, concrete, and other porous substrates.
- High fluorine content resins of various types for optical fiber cladding and anti-fouling applications.

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- Functional resins for powder and liquid coating applications, based on the copolymerization of fluorinated monomers and low levels of nonfluorinated monomers with cross-linkable functional groups.

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